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Process for the continuous manufacture of tubular membrane

Description

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The invention relates to a process for the continuous manufacture of tubular composite or multi-layer membranes formed as tubes or hoses, in the following related to as membrane tubes.

- 10 For any application a multitude of tubular membranes is assembled in a membrane module. General known types of such modules are the hollow fiber module, the capillary module, and the tubular module. The respective differences are due to the variation of the diameter of the tubular membranes. The diameters of hollow fiber membranes range between 30 to 100 micron, those of capillary membranes between 0.2 to 3 mm, and those for membrane tubes between 4 to 50 mm.
- 15 In hollow fibers the transmembrane flux is directed from the outside to the inside, in capillary membranes from the outside to the inside as well as in the reverse direction, and in tubular membranes mostly from the inside to the outside.
- 20 It is known in the art to manufacture membrane tubes with the active layer on the inside discontinuously by introducing a cone shaped body, the "bobby" into a vertically arranged tube. Above the "bobby" the respective polymer solution is poured from which the membrane will be formed. By moving the "bobby" through the tube a thin film of the polymer solution is distributed on the inner wall
- 25 of the tube, said film being precipitated and solidified by means known in the art. The thus formed membrane can be removed from the tube and supported by any means known in the art. More often the membrane film is directly cast on a porous carrier material, either by a "bobby" or the polymer solution is distributed on the inner wall of the tube by passing a gas bubble through the tube. This method is

known as "hydrocasting". The porous carrier material has to withstand all following steps.

It is further known in the art to manufacture membrane tubes with the active layer
5 on the inside continuously by applying a polymer dope by means of an annular
nozzle to a carrier material. According to US-PS 3 601 159 said carrier can be
formed by winding several layers of suitable material around a mandrel. The nozzle
is located at the end of said mandrel. Another possibility is given by forming a
strip of the carrier material into a hose the overlap of which are then glued or
10 welded together.

Capillary membranes are formed from polymer solutions by a so called "spinneret",
a device comprising an annular nozzle around a central needle. Through an
additional nozzle in said inner needle a precipitating agent for the polymer solution
15 can be introduced into the inner volume of the capillary. Bundles of such capillaries
are glued together at both ends and housed in a pressure vessel. It is important
to obtain a crack- and stress-free scaling; furthermore the openings of the capillaries
must not be blocked during cutting. The production of hollow fiber membranes
is similar to the production of textile hollow fibers. They can be formed by
20 wet spinning, dry spinning, or melt spinning processes. The center of the spinneret
is formed by a hollow needle, through which an inert gas or liquid is introduced
in order to prevent collapsing of the fiber. During or following the spinning
process the fibers may be stretched to the wanted diameter. Very fine hollow fiber
membranes are charged from the outside, at larger diameters the feed flow can
25 pass through the interior of the hollow fiber.

Depending on the conditions during the formation the active layer of the tubular
membrane, responsible for the separation, will be continuously porous with a
symmetric or asymmetric pore structure. In special cases a dense, essentially pore
30 free structure can be formed.

- It is a common property of the aforesaid membranes to comprise of one distinct material only, besides an additional carrier layer. Said distinct material may be inorganic or an organic polymer. Therefore these membranes are referred to as integral membranes. On to the carrier layer which may be a woven or non-woven fabric the integral membrane is applied, and the carrier improves the mechanical strength and handability of the membrane. The carrier layer shows relatively large pores which allow for an unhindered flow. Preferentially, as the other parts of the membrane, the carrier layer is resistant against chemicals and higher temperatures.
- 10 Tubular membranes comprising an integral membrane on a carrier layer can be formed by winding a narrow stripe of the carrier material around a mandrel thus forming a hose or tube, and butt welding or overlap welding the edges by heat or ultrasound. In a following step the hoses or tubes are coated, e.g. by a polymer solution. Preferentially the polymer solution is applied to the inner surface of the
- 15 tube, as the latter may collapse when an outside pressure is applied. Therefore an opening exists at the end of the mandrel through which the polymer solution is applied to the inner surface of the tube. By immersion into a precipitation bath the membrane is then formed. Thus first a hose or tube is formed from the carrier material which is then uniformly coated on the inside. Any defects originating from
- 20 imperfect welding shall be thus coated and sealed.

Following the above described continuous methods only integral or single-layer tubular membranes can be produced, as after coating of the carrier with the polymer solution and formation of the membrane any further coating can be applied

25 only discontinuously to separate and distinct pieces of the membrane. Technically this is disadvantageous and uneconomical. The integral tubular membranes as described are mainly used in microfiltration, ultrafiltration and nanofiltration processes.

- 30 For the processes of reverse osmosis, pervaporation/ vapor permeation, and gas separation preferentially multi-layer membranes are utilized, which comprise at

least two layers of different chemical composition, in addition to the carrier layer. In general such composite membranes comprise a first porous sublayer which determines mainly the mechanical strength of the membrane (support layer), and adjacent to the sublayer a second layer of a chemically different material which
5 mainly determines the separation characteristics of the membrane (separating layer). The separating layer may be microporous or dense and pore-free. Membranes for Reverse Osmosis in general comprise a microporous separating layer, having pores with diameters in the range between 10 to 1000 Å. Membranes used in Pervaporation/ Vapor Permeation and Gas Permeation may still have a certain
10 number of pores with diameters of 10 Å or below, nevertheless they are referred to as dense or pore-free. Technically the dense or pore-free membranes are distinguished from the microporous ones as they separate according to the Solution-Diffusion-Mechanism. Examples of such useful dense separating layers are disclosed in EP-B-0 096 339, e.g. made from polyvinylalcohol or polyvinylalcohol
15 copolymers. By means of an aqueous solution of said polymer, which may contain additional cross-linking agents for polyvinylalcohol a thin layer is applied to a support layer, which is then subjected to a drying and heat treatment step in order to cross-link the polyvinylalcohol. To those skilled in the art further composite membranes are known, useful for the processes mentioned above.

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In principle tubular membranes can be formed from flat sheet composite membranes by the above described method. However, the glue lines and especially welding seams of membrane tubes thus formed will show defects and leakages as it is not possible to weld at least two layers of different materials (separating
25 layer, support layer and eventually carrier layer) uniformly and defect free. It is the task of the present invention to present a solution to this problem.

The present invention thus relates to a process for the continuous production of composite membrane tubes, comprising a porous sublayer (support layer), mainly
30 determining the mechanical strength of the membrane, and adjacent to that a second layer of a material of different chemical nature, said second layer mainly de-

termining the separation properties of the membrane (separating layer), said process comprising winding a respective flat sheet composite membrane lengthwise or spirally into a tubular form, the separating layer of said membrane facing to the inside, welding or gluing the edges of said membrane together, either overlapping
5 or by butt welding, and applying on the inside of said butt seam or overlapping area a strip of a sealing material which can be solidified and finally solidifying said sealing material.

The support layer and the separating layer of a composite membrane are made
10 from materials of different chemical nature. Such membranes which are made and used as flat sheets for the separation of liquid mixtures by Pervaporation/ Vapor Permeation or Gas Separation are disclosed by e.g. EP-B-0 096 339. For the method according to the present invention flat sheet composite membranes are preferred comprising an additional carrier layer of a woven or non-woven fabric.

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The membrane tubes according to the present invention have diameters in the range between 4 to 50 mm, preferentially between 8 to 30 mm, whereby diameters between 12 to 25 mm have proven to be advantageous.

20 Preferentially the membrane tube is formed by spirally winding a flat sheet composite membrane around a mandrel or shaft, whereby the winding may overlap or form butt seams. In the final membrane tube the separating layer forms the inside surface. In a preferred arrangement comprising a carrier layer the order of the layers from the inside to the outside of the membrane tube is as follows: Separating
25 layer, support layer, carrier layer. Welding is effected by e.g. ultrasound or heat. When butt welding is preferred an additional strip of material is applied to the seam which can be efficiently be welded or glued to the material with which it is in contact, and said material is then glued or welded to the material of the membrane. When a membrane comprising a carrier layer is processed, the carrier layer
30 made e.g. from a woven or non-woven fabric, said additional strip of material is preferentially chosen from the same material as that of the carrier layer. Hereby it

is of no concern whether the other layers are totally welded or glued, as any defects will be sealed by the application and solidification of the later applied sealing material. The width of said strip of material is chosen in such a way that a permanent fixation of the butt weld seam is effected, e.g. 2 to 10 mm, or 2 to 4
5 mm.

In a next step a stripe of a sealing material which can be solidified is applied from the inside of the membrane tube to the butt seam or the area of overlapping, respectively, and solidified. The sealing material, preferentially a polymer, has to
10 exhibit a good adhesion to the separating layer of the membrane, its thermal and chemical resistance have to be similar to that of the separating layer. Thus it is preferred to use the polymer of the separating layer as the sealing polymer. The sealing polymer can then be treated and cross-linked by the same means as the separating polymer of the flat sheet membrane. Examples of useful sealing poly-
15 mers are polyvinylalcohol, dissolved in water, for polyvinylalcohol separating layers; polyurethane, dissolved in ketones or ester, for polyurethane separating layers; and siloxanes, dissolved in ketones, for siloxane separating layers.

The sealing material is applied from the inside of the membrane tube onto the butt
20 seam or the area of overlapping by means of a nozzle, coupled to a respective control of the speed by which the membrane tube is formed. The application of the sealing material is controlled in order to coat and seal the butt seam or the area of overlapping in a width of 1 to 2 mm, or wider, if required. Preferentially said nozzle is located on the mandrel or shaft around which the membrane tube is formed
25 and welded or glued. Thus formation of the membrane tube, welding or gluing and application of the sealing materials is effected in a single operation.

In order to improve its mechanical stability one or more drainage layers, in addition to the carrier layer can be applied to the membrane tube, as is known in the
30 art.

According to the process of the present invention membrane tubes can be manufacture from flat sheet composite membranes, the membrane tubes being free of defects and exhibiting the same selectivity as the respective flat sheet membrane.

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